

Natural orbital phase dependence in (TD)DMFT?

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Introduction

Although many successes have been reported for time-dependent density functional theory (TDDFT), it has some significant failures:

- **Vanishing excitation energy.** For example: the lowest $^1\Sigma_u^+$ of H_2 .
- **Lack of double excitations.** For example: the lowest $^1\Sigma_g^+$ of H_2
- **Charge transfer (CT) excitations.** For example: the lowest $^1\Sigma^+$ of HeH^+

Density matrix functional theory (DMFT) has been a great improvement for ground state energies of dissociating molecules. Time-dependent DMFT (TDDMFT) could also improve these problematic TDDFT excitations, which are related to dissociating systems.

TDDMFT

The time-dependent one-matrix is defined as

$$\begin{aligned} \gamma(\mathbf{x}, \mathbf{x}'; t) &\equiv \langle \Psi | \hat{\psi}^\dagger(\mathbf{x}') \hat{\psi}(\mathbf{x}) | \Psi \rangle \\ &= \sum_k n_k(t) \phi_k(\mathbf{x}t) \phi_k^*(\mathbf{x}'t), \end{aligned}$$

where

- $n_k(t)$ are the occupation numbers
- $\phi_k(\mathbf{x}t)$ are the natural orbitals (NOs)

TDDMFT can straightforwardly be derived from the EOM of the one-matrix. In a basis set we have

$$\begin{aligned} i\dot{\gamma}_{ki}(t) &= \langle \Psi | [\hat{c}_i^\dagger(t) \hat{c}_k(t), \hat{H}(t)] | \Psi \rangle \\ &= \sum_r (h_{kr}(t) \gamma_{ri}(t) - \gamma_{kr}(t) h_{ri}(t)) + \\ &\quad (W_{ki}^\dagger(t) - W_{ki}(t)). \end{aligned}$$

The matrices $\mathbf{W}(t)$ are defined as

$$W_{kl}(t) \equiv \sum_{rst} \Gamma_{krst}(t) w_{tsrl}(t),$$

with the two-matrix and two-electron integrals defined as

$$\begin{aligned} \Gamma_{klrs}(t) &\equiv \langle \Psi | \hat{c}_s^\dagger(t) \hat{c}_l^\dagger(t) \hat{c}_l(t) \hat{c}_k(t) | \Psi \rangle \\ w_{klrs}(t) &\equiv \int d\mathbf{x} \int d\mathbf{y} \phi_k^*(\mathbf{x}) \phi_l^*(\mathbf{y}) w(\mathbf{x}, \mathbf{y}) \phi_r(\mathbf{y}) \phi_s(\mathbf{x}) \end{aligned}$$

After some manipulations and using the adiabatic approximation $W[\gamma](t) \approx W[\gamma(t)]$ can be written in the following matrix form

$$\begin{pmatrix} \omega \mathbf{1} & \mathbf{A}^+ & \mathbf{0} \\ \mathbf{A}^- & \omega \mathbf{1} & \mathbf{C} \\ \mathbf{0} & \mathbf{D} & \omega \mathbf{1} \end{pmatrix} \begin{pmatrix} \delta\gamma^R(\omega) \\ i\delta\gamma^I(\omega) \\ \delta n^R(\omega) \end{pmatrix} = \begin{pmatrix} \mathbf{0} \\ \delta\mathbf{v}^R(\omega) \\ \mathbf{0} \end{pmatrix},$$

The submatrices relate to the derivatives of the energy functional as

$$\begin{aligned} \mathbf{A}_{klba}^\pm &\sim \frac{\delta^2 E}{\delta\phi_k(\mathbf{x}) \delta\phi_b(\mathbf{x}')} + \text{arb. complex conjugations} \\ \mathbf{C}_{kla} &\sim \frac{\partial}{\partial n_a} \frac{\delta E}{\delta\phi_k(\mathbf{x})} + \text{c.c.} \\ \mathbf{D}_{kba} &\sim \frac{\delta}{\delta\phi_b(\mathbf{y})} \left(\frac{\delta E}{\delta\phi_k(\mathbf{x})} \phi_k(\mathbf{x}) - \frac{\delta E}{\delta\phi_k^*(\mathbf{x})} \phi_k^*(\mathbf{x}) \right) + \text{c.c.} \end{aligned}$$

Motivation for phases I

For the singlet two-electron system almost the exact functional is known, by diagonalising the spatial part of the two-electron wavefunction

$$W[\phi, n] = \min_{\{f\}} \frac{1}{2} \sum_{rs} f_r f_s \sqrt{n_r n_s} w_{rrss},$$

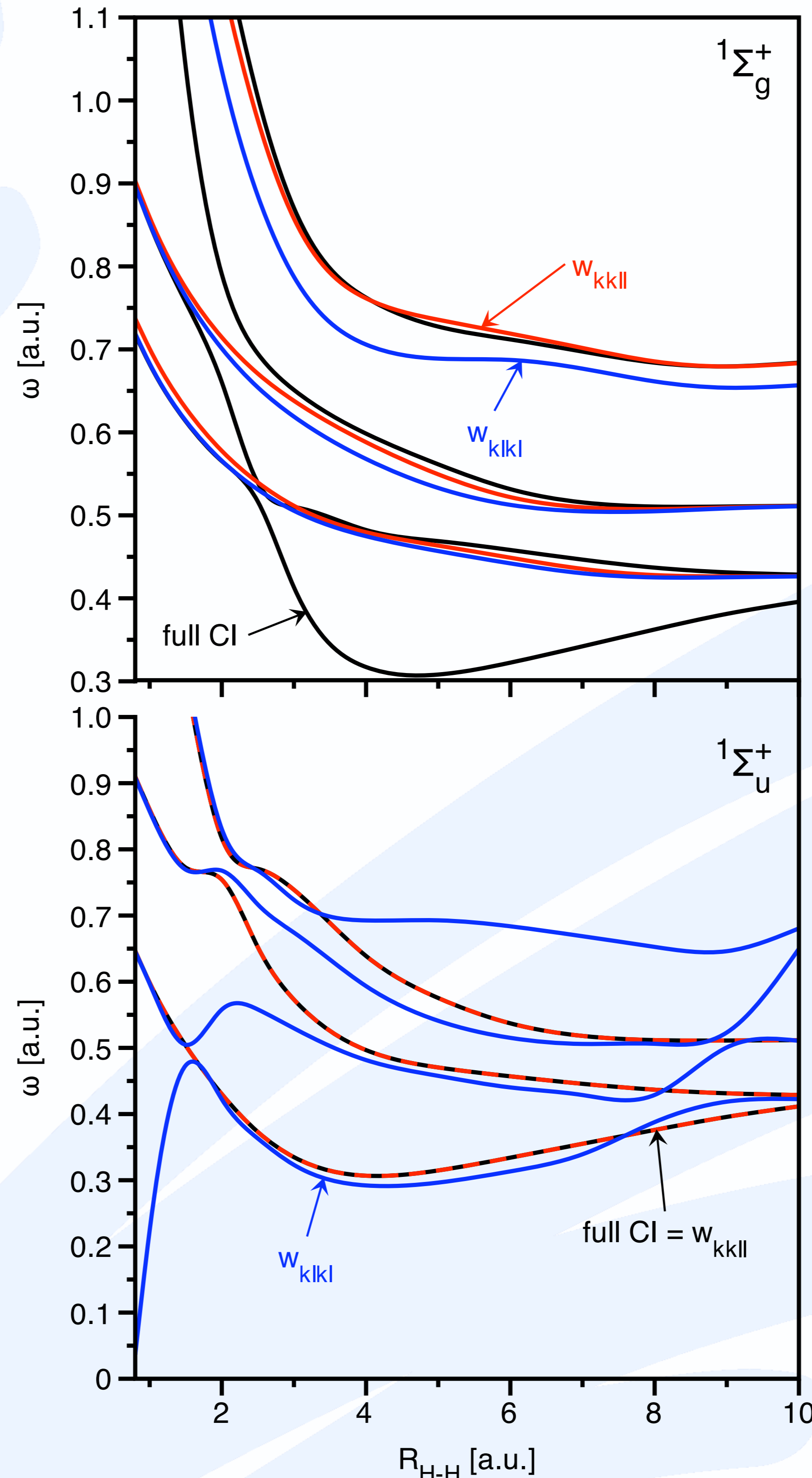
There are two ways to write approximate the explicit two-electron functional which are equivalent for real NOs

$$W[\phi, n] = \frac{1}{2} \sum_{rs} f_r f_s \sqrt{n_r n_s} w_{rrss} \quad (\text{a})$$

$$W[\phi, n] = \frac{1}{2} \sum_{rs} f_r f_s \sqrt{n_r n_s} w_{rsrs}. \quad (\text{b})$$

A good choice for the phase factors turns out to be $f_1 = 1$ and $f_r = -1 \forall r > 1$ in practice. Since the functional should be phase invariant, definition (b) is the only proper DMFT functional.

However, the matrix \mathbf{A} contains second order derivatives with respect to ϕ and ϕ^* . Therefore, both approximations give a different response matrix \mathbf{A}^\pm . It turns out that violation of phase invariance gives better results. An example is shown for the lowest $^1\Sigma_g^+$ and $^1\Sigma_u^+$ excitations for dissociating H_2 in the figure below



The first $^1\Sigma_g^+$ and $^1\Sigma_u^+$ excitation energies of H_2 in a p -cc-pVTZ basis set as a function of the interatomic separation R . The black lines are the exact within the basis set. The red lines are the adiabatic results using w_{kkll} integrals (definition (a)). The results with the w_{kkik} integrals (definition (b)) are shown in blue.

Motivation for phases II

The TDDMFT response equations in the adiabatic approximation

Since the energy functional should be invariant under NO phase transformations, we have

$$\mathbf{D} = 0.$$

This immediately gives $\delta n_k(\omega) = 0$. Comparing to static response¹, where $\delta n_k \neq 0$, we immediately see that

$$\lim_{\omega \rightarrow 0} \delta n_k(\omega) \neq \delta n_k^{\text{static}}$$

Allowing for a phase dependence, we could have

$$\mathbf{D} \neq 0$$

and potentially solve the static limit problem.

EOM for the NOs

For time-independent DMFT it is possible to define an effective NO equation²

$$(\hat{h} + \hat{v}^{\text{eff}}) \phi_k(\mathbf{x}) = \epsilon \phi_k(\mathbf{x})$$

where the effective potential \hat{v}^{eff} is related as

$$v_{kl}^{\text{eff}} \sim \begin{cases} W_{kl}^\dagger - W_{kl} & \text{for } k \neq l \\ \frac{\partial W}{\partial n_k} & \text{for } k = l \end{cases}$$

Suppose there would exist an EOM of the form

$$(\hat{h}(t) + \hat{v}^{\text{eff}}(t)) \phi_k(\mathbf{x}t) = i \partial_t \phi_k(\mathbf{x}t)$$

Augmenting the NO equation with the EOM for the occupation numbers and applying linear response within the adiabatic approximation, we can write down the following matrix equation

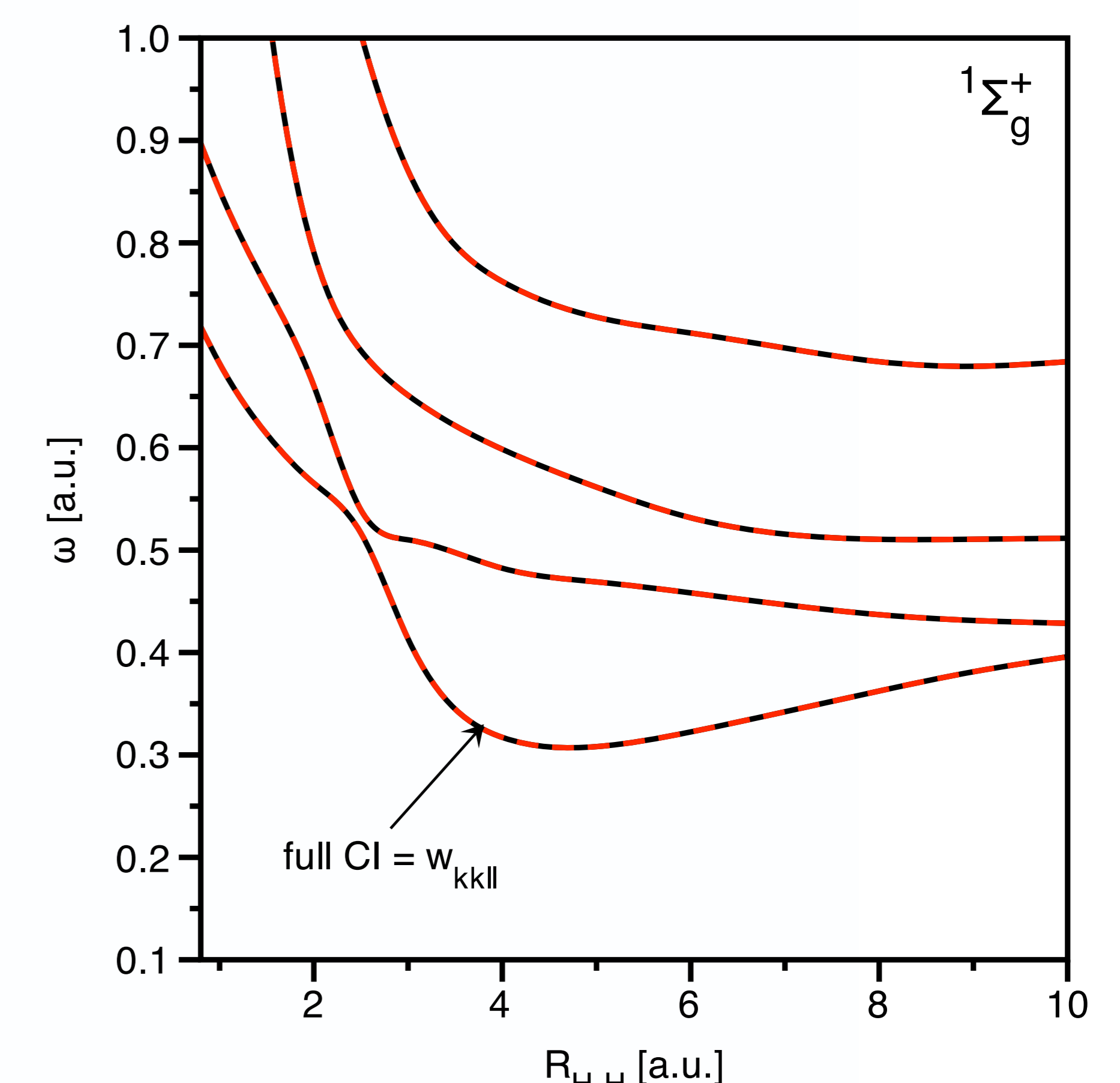
$$\begin{pmatrix} \omega \mathbf{1} & \mathbf{0} & \mathbf{A}^+ & \mathbf{A}^+ \\ \mathbf{0} & \omega \mathbf{1} & \mathbf{A}^+ & \mathbf{A}^+ \\ \tilde{\mathbf{A}}^- & \tilde{\mathbf{C}} & \omega \mathbf{1} & \mathbf{0} \\ \tilde{\mathbf{C}}^T & \tilde{\mathbf{W}} & \mathbf{0} & \omega \mathbf{1} \end{pmatrix} \begin{pmatrix} \delta\gamma^R(\omega) \\ \delta\mathbf{n}(\omega) \\ i\delta\mathbf{U}^I(\omega) \\ i\delta\mathbf{U}^D(\omega) \end{pmatrix} = \begin{pmatrix} \mathbf{0} \\ \mathbf{0} \\ \delta\mathbf{v}^R(\omega) \\ \delta\mathbf{v}^D(\omega) \end{pmatrix},$$

where the matrix $\tilde{\mathbf{W}}$ as approximately

$$\tilde{W}_{ka} \sim \frac{\partial^2 E}{\partial n_k \partial n_a}$$

These equations have a couple of convenient properties

- The static limit is equal to the static response: $\lim_{\omega \rightarrow 0} \delta n_k(\omega) = \delta n_k^{\text{static}}$
- Singlet two-electron system are exact if we use the w_{kkll} integrals (see figure below). dependent coupling matrix.



The first $^1\Sigma_g^+$ excitation energies of H_2 in a p -cc-pVTZ basis set as a function of the interatomic separation R . The black lines are the exact within the basis set and the red lines are the results if we use the w_{kkll} integrals in the response equations derived from the effective NO equation.

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References

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